



Project Summary

Chemical Characterization of Polynuclear Aromatic Hydrocarbon Degradation Products from Sampling Artifacts

J. C. Chuang, S. W. Hannan, and L. E. Slivon

The objective of this study was to characterize the polar components, mainly polynuclear aromatic hydrocarbon (PAH) derivatives, in air samples and to determine whether these compounds are from sampling artifacts or from the sampled air.

A literature survey was conducted to review the studies about polar PAH derivatives found in the air. In general, there is limited chemical and biological information for polar PAH available in the literature. Most of the studies revealed that PAH and NO₂-PAH cannot totally account for indirect- and direct-acting mutagenicity in air samples. The polar fractions of air samples did show a significant amount of mutagenic activity. The authors concluded that more studies are needed in this area to determine the polar components responsible for the activity.

A storage stability study of PAH collected on quartz fiber filters and XAD-2 resin was conducted. The results showed that some reactive PAH including acenaphthylene and cyclopenta[c,d]pyrene partially decompose to naphthalene and pyrene dicarboxylic acid anhydrides after storage for 30 days in the dark at room temperature between sampling and extraction.

The determination of unknown polar components in air samples is a

complex task. The NCI GC/MS method is a very sensitive technique for the determination of NO₂-PAH and oxygenated PAH (OXY-PAH), however, analyses of the standards are required to confirm the identification. The NCI and PCI MS/MS techniques can provide characteristic fragmentation patterns for NO₂-PAH and OXY-PAH, respectively. More studies are needed to evaluate a fast screening method to determine these compounds with MS/MS.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Polynuclear aromatic hydrocarbons (PAH) have been extensively studied in recent years and have received increasing attention in the investigation of air pollution. Many PAH are known to be animal carcinogens, mutagens, or both. Most PAH are likely to react with air, sunlight, and other pollutants (O₃, NO_x, and SO₂) in the atmosphere to form PAH derivatives because PAH can absorb light at the wavelengths found in sunlight (>300 m). The PAH derivatives present

in air arise partly from various combustion emissions sources, in addition to atmospheric transformation. Degradation products of PAH may also be formed as artifacts of sample handling or sample storage conditions. Recently, Battelle conducted a study which showed that the amount of particle-bound cyclopenta[c,d]pyrene decomposes to about half of its original value after storage for 30 days in the dark at room temperature. In general, little is known about the PAH degradation products formed as sampling artifacts. However, it has been demonstrated that PAH degradation products may exhibit a higher mutagenic activity than their parent PAH. Therefore, it is important to determine whether those PAH derivatives are sampling artifacts or were actually present in the air sampled.

Many studies have demonstrated that PAH and NO₂-PAH cannot totally account for the indirect- and direct-acting mutagenicity of air samples; other classes of compounds must also contribute to the activity. In fact, the polar fractions of air samples have shown very strong direct-acting mutagenicity. In some cases the activity of the polar fraction is greater than 50 percent of the total activity. The authors expect that many of the PAH derivatives, such as NO₂-PAH and oxygenated PAH (OXY-PAH), are present in the polar fractions. However, only limited biological and chemical information is available for these polar components in the air. Therefore, a study was carried out to characterize PAH degradation products in air.

The objective of this study was to characterize the polar components, mainly PAH derivatives, in air samples and to determine whether these compounds are sampling artifacts or are from the sampled air. This study consisted of the following subtasks:

1. Conducting a literature survey to review the studies about polar PAH derivatives found in the air,
2. Performing a storage stability study of PAH collected on quartz fiber filters and XAD-2 resin,
3. Conducting chemical characterization of the day-0 and day-30 samples in an attempt to determine the PAH degradation products produced due to storage, and
4. Preparing the samples from the stability study for bioassay.

Procedure

A literature survey was performed by a computer search of five data bases:

Chemical Abstracts (1967-1986), APTIC (1966-1978), NTIS (1970-1986), Medline (1970-1986), and Cancerline (1970-1986). Abstracts or citations considered most relevant to the subject area were reviewed and divided into two subsets: analytical and biological data, for further evaluation. Photocopies of some important articles were also obtained to allow a more detailed evaluation.

Two sets of four samplers were located in parallel approximately two feet apart, with the four samplers separated from each other by about one foot. Quartz fiber filters and XAD-2 resin in series were used in all samplers. Ambient air was sampled for 24 hours at 6.7 cfm flow rate. After collection, the samples were stored as replicate pairs in the dark at room temperature for 0, 10, 20, and 30 days before extraction. The sample extracts were divided into two portions: portion I used for chemical analysis and portion II used for bioassay analysis. Portion I of each XAD-2 sample was fractionated into four fractions prior to chemical analysis. The sample extracts and fractions were analyzed by electron impact (EI) and negative chemical ionization (NCI) gas chromatography/mass spectrometry (GC/MS), as well as, triple quadrupole mass spectrometry.

Results

The results of the literature survey showed that besides PAH, nitro PAH, and hydroxy-nitro-PAH, the polar fractions of the air particulate extracts have also revealed mutagenic activity. It appeared that oxygenated PAH (OXY-PAH) may have also contributed to the biological activity in other environmental samples. However, there is a lack of mutagenicity and carcinogenicity data on individual OXY-PAH in the literature, and more research should be directed to studies of the biological activity of OXY-PAH. Analytical methods including EI and CI GC/MS or high pressure liquid chromatography (HPLC) have been used to determine polar PAH including NO₂-PAH and OXY-PAH. The analytical methods to determine NO₂-PAH have been well established compared to methods for other polar PAH. No systematic efforts have been made to determine OXY-PAH. In most cases, isomer-specific identification of OXY-PAH was not possible by GC/MS alone. A combination of different analytical techniques was used to determine isomeric OXY-PAH. Furthermore, the absence of authentic standards

prevented the positive identification isomeric OXY-PAH. The ability to determine specific isomeric compounds is important, because some isomeric compounds have quite different biological activity. Therefore, more investigations are needed.

The results of the stability study revealed that the PAH vapors collected on XAD-2 resin appear to be stable over the 30-day storage, except for acenaphthylene, indicating a slight decreasing concentration trend. The results also indicated that most particulate-bound PAH, except for cyclopenta[c,d]pyrene, were not adversely influenced by a 30-day storage time. Both acenaphthylene and cyclopenta[c,d]pyrene, having similar structure with vinylic bridges, are reactive PAH and can be expected to show storage instability over 30 days.

It is likely the relatively localized double bonds in these reactive PAHs oxidize to the corresponding PAH dicarboxylic acid anhydrides during storage. Indeed, the levels of acenaphthylene and pyrene dicarboxylic acid anhydrides from the day-30 samples were more than 1.5 times those of the day-0 samples. This finding clearly suggests that the acenaphthylene and cyclopenta[c,d]pyrene partially decompose to naphthalene and pyrene dicarboxylic acid anhydrides during storage. There were a few other components including nitrogen-containing compounds and OXY-PAH that revealed increasing concentration trends during 30-day storage. The tentatively identified hydroxynitropyrene isomer and 2/3 nitrofluoranthene show decreasing concentration trends after storage. The authors also found a few unknown components present only in the day-0 samples and not in the day-30 samples.

The negative chemical ionization (NCI) MS/MS analysis of the NO₂-PAH revealed characteristic collisionally activated dissociation (CAD) patterns which are M⁻ (M-NO)⁻, and NO₂⁻. The hydroxynitropyrene showed the same pattern of fragmentation ions as the NO₂-PAH, as well as (M-NO-OH)⁻. However, the estimated detection sensitivity of NCI MS/MS, in general, is lower than the conventional NCI GC/MS technique. The detection sensitivity could be improved by performing the MS/MS at optimum instrumental sensitivity. More investigations need to be carried out in order to obtain a true comparison of detection limits for NO₂-PAH and OXY-PAH for those two techniques.

CI GC/MS and NCI GC/MS/MS. There were no characteristic fragmentation patterns for OXY-PAH standards observed in the NCI MS/MS analysis. However, a specific CO neutral loss was observed in the CAD spectra of OXY-PAH, including polynuclear aromatic aldehydes, polynuclear aromatic ketones and polynuclear aromatic acid anhydrides. More studies are needed to optimize the detection sensitivity.

Conclusions and Recommendations

In conclusion, there is limited chemical and biological information on PAH derivatives in air with the exception of NO₂-PAH. Therefore, more studies are needed in this area to determine the polar components responsible for the mutagenic activity in air samples.

The results of the stability study showed that the reactive PAH acenaphthylene and cyclopenta-[c,d]pyrene, partially decompose to naphthalene and pyrene dicarboxylic acid anhydrides after storage before extraction for 30 days in the dark at room temperature. One of the degradation products, pyrene-3,4-dicarboxylic acid anhydride, has been reported as a direct-acting mutagen. Therefore, future air sampling studies should involve a minimum of sample handling and storage to reduce the degradation of reactive PAH.

The determination of unknown polar components in air samples is a complex task. The EI GC/MS analyses of the unfractionated filter samples did not detect PAH derivatives. Even though the NCI GC/MS method is a very sensitive method for the determination of NO₂-PAH and OXY-PAH, analyses of standards are required to confirm the identification. The authors conclude that more investigation, such as fractionation of the sample and evaluation of different analytical methods is needed to characterize the polar components in air samples.

The authors recommend that a study should be performed to investigate the chemical and biological characteristics of a series of reactive PAH and their degradation products and to determine the extent of mutagenic activity of PAH degradation products from sampling artifacts.

J. C. Chuang, S. W. Hannan, and L. E. Slivon are with Battelle Columbus Division, Columbus, OH 43201.

Nancy K. Wilson is the EPA Project Officer (see below).

The complete report, entitled "Chemical Characterization of Polynuclear Aromatic Hydrocarbon Degradation Products from Sampling Artifacts," (Order No. PB 88-133 616/AS; Cost: \$14.95, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711*

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use \$300

EPA/600/S4-87/039 0000329 PS

U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604

